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## (54) PREPARATION OF ZEOLITE A IN EXTRUDED FORM

(71) We, W.R. GRACE & CO., a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of Grace Plaza, 1114 Avenue of the Americas, New York, New York 10036, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a clay based binderless extrusion process for preparing synthetic crystalline zeolites having an effective pore size of 4 to 5Å which are characterized by improved adsorption capacity, crushing strength, selectivity, adsorption-desorption rate characteristics and desirable pore size distributions. The product can also retain its integrity in boiling water.

Micro-crystalline adsorbents of the zeolite type are crystalline aluminosilicates with a three-dimensional structure of silica-alumina tetrahedra. This zeolite structure is characterized by a repeating three-dimensional network of large open aluminosilicate cages that are connected by smaller uniform openings in pores. Certain of these microselective adsorbents have been prepared synthetically from sodium aluminate and sodium silicate. After synthesis these large cavities are filled with water which can be driven off by heating without collapsing the cage. When dehydrated these cavities can readorb large quantities of water or other vapour at low partial pressure. Due to the uniform structures or pore openings connecting the aluminosilicate cavities these zeolites exhibit the unique property of excluding larger molecules from the cavities and allowing small molecules to pass through and be adsorbed thereby acting as microselective adsorbents from molecules according to their size and shape. One type of zeolite and the type with which the present invention is concerned, is zeolite A, which can be synthesised to have sodium as cation in which case it has a pore size of 4 angstrom units, or which after synthesis can be ion-exchanged to have calcium as cation in which case it has a pore size of 5 angstrom units.

Because the zeolites are normally recovered from the manufacturing process as fine powders it is necessary to form the zeolites into nodular structures that can be packed into fixed beds for adsorption of gases or liquids from a stream. This is normally done by binding the zeolites with a material such as clay. The disadvantage of such a process however is that the clay is inactive and, thus, from 15 to 20% of the bed (depending on the percentage of clay used as a binder) is inactive and, also, increases the degree of non-selectivity depending on clay employed.

U.S. Patent 3,119,659 discloses a process for preparing a so-called binderless sieve in which clay is converted to zeolite by subsequent treatment to convert the clay binder to zeolite. This process involves a crystallization step in which the nodules are heated in a bath of sodium hydroxide solution to convert the clay binder to the zeolite.

It has been found that the process for preparing type A zeolites can be greatly simplified and some of the steps in the conventional processes eliminated by the following process of the invention. The metakaolin powder (which suitably, is blended with a pilling aid) is mixed with sufficient sodium hydroxide to provide 80 to 120 weight percent of the theoretical (stoichiometric) amount needed to convert the metakaolin to zeolite, optionally with 0.1 to 1%, by weight based on the alumina, of nucleation centres. The mixture is then extruded and the resultant extrudates are crystallised by heating at 80 to 110°C for 2 to 8 hours, preferably in a hot sodium hydroxide solution containing 1 to 5, most preferably about 3%, by weight, sodium hydroxide or in hot water, to produce a zeolite of pore size 4Å. After the reaction is

complete the extrudates are washed to remove excess sodium hydroxide. If the 5Å calcium zeolite is desired the washed product from this step is exchanged with a solution of a calcium. The 4Å product or 5Å product can be exchanged or further exchanged with a solution of a magnesium salt or rare earth metal salt. The exchange can be effected at any stage after the washing. The extrudates are dried at a temperature of 200 to 400°F to a moisture content of 5-15%, usually 8-15%, preferably 10%, by weight, and calcined at a temperature of 400 to 1100°F., to the moisture content of 1-5%, preferably 2-3% by weight.

In the preferred process shown schematically in the accompanying drawing, the first step of the process is the blending of the clay with a suitable pilling aid, most preferably in a proportion of 1 to 3% by weight. The clay is kaolin that has been calcined to transform it to metakaolin. A preferred pilling aid is a long chain fatty acid pilling aid such as that commercially available under the tradename of "Sterotex".

In the next step of the preferred process the blend of metakaolin and pilling aid is mixed in an intensive mixer with the proper amount of sodium hydroxide needed to convert the clay to the zeolite. The sodium hydroxide is added in this step, preferably as a solution containing 30 to 55 weight percent NaOH, to provide 80 to 120% of the theoretical amount required to convert the metakaolin to the zeolite.

If it is desired to add nucleation centres, they are added at this stage. The nucleation centres are not part of this invention. The method for their preparation is described in U.S. Patents 3,769,386 and 3,639,099; in brief, the nucleation centres are a slurry of particles formed from a mixture of the type used for crystallisation of zeolites, the particles having the chemical composition of zeolites (not necessarily of zeolite A) but a particle size so fine that they are amorphous, i.e. do not exhibit the crystal structure which is characteristic of zeolites when examined by x-ray diffraction techniques. The metakaolin-sodium hydroxide and optionally nucleation centres are mixed thoroughly in an intensive mixer for a period of  $\frac{1}{2}$  to 1 hour.

In the next step of the preferred process the mixture is extruded through a conventional extruder. The extrudates are nodules  $\frac{1}{16}$  to  $\frac{1}{4}$  inches long and  $\frac{1}{16}$  to  $\frac{1}{4}$  inches in diameter, most preferably  $\frac{1}{16}$  -  $\frac{1}{8}$  inches long and  $\frac{1}{16}$  -  $\frac{1}{8}$  inches in diameter.

The next step of the preferred process is the crystallization step. The mixture is crystallized to type A zeolite by heating the extrudates in a hot solution containing 1 to 5% sodium hydroxide, preferably about 3% or in hot water. Preferably the hot aqueous solution contains nucleation centres, which can have been added previously, in the preferred proportions mentioned above. This crystallisation is carried out at a temperature of 80 to 120°C., preferably about 100°C. for a period of 2 to 8 hours, preferably about 4 hours. The extrudates are then washed to remove excess sodium hydroxide. If the extrudates are to be converted to the calcium or other form, e.g. magnesium or rare earth, they can be exchanged with the desired solution at this stage and rewashed.

The final step of the process is the drying and calcining step.

The invention is illustrated by the following specific but non-limiting examples

#### Example 1

This example illustrates a plant process for preparing the unified clay based binderless extruded type A zeolite.

In a first run (a), a total of 3500 lbs of metakaolin was blended with 35 lbs of Sterotex, (a commercially available pilling aid). The mixture was then transferred to a Sigma mixer and a total of 1386 lbs of sodium hydroxide (110% of the theoretical amount required to convert the metakaolin to type A zeolite) was added as a solution containing about 45 weight percent sodium hydroxide in water. This amount was equivalent to 40 lbs of 100% sodium hydroxide per 100 lbs. of metakaolin. A total of 350 lbs of a slurry of nucleation centres (containing sufficient nucleation centres to provide 0.26 weight percent based on the weight of the alumina in the metakaolin) was added. The clay, sodium hydroxide and nucleation centres were mixed for a period of  $\frac{1}{2}$  to 1 hour in the Sigma mixer. At the end of this time the product was extruded to form  $\frac{1}{8}$  inch long extrudates about  $\frac{1}{8}$  inch in diameter. The extrudates were then transferred to a reactor and crystallized in a solution containing about 3 weight percent sodium hydroxide. The crystallization was carried out at a temperature of about 210°F. for a period of 4 hours. At the end of this time the extrudates were washed with water for 4 hours and dried to the moisture content of 10 weight percent at a temperature of about 150°C. They were then calcined at a temperature of 1000°F for 2 hours.

Another run (b) was made starting with blend containing 3500 lbs of metakaolin and 35 lbs of Sterotex. The blended powder was transferred to Sigma mixer and a total of 1386 lbs of sodium hydroxide (110% of the theoretical amount required to convert the metakaolin) was added as a solution diluted to about 40 weight percent sodium hydroxide. No nucleation centres were added in this run. Thereafter, the procedure of run (a) was followed.

*Example 2*

Several of properties of the product of run (a) of Example 1 were compared with a conventional 4A molecular sieve commercially available from Davison Chemical Division of W.R. Grace and Co. and designated "Davison R". The product was also compared with a commercially available 4A molecular from the Linde Division of Union Carbide Corporation in the form of 1/8th inch extrudates and designated "Linde R". "Linde" is a Registered Trade Mark. The product was also compared with a binderless 4A molecular sieve designated "Davison BL". The data are set out in Table 1 below.

*Table 1*

**COMPARISON OF KEY PROPERTIES  
4A MOLECULAR SIEVES**

	Davison, R	Linde, R	Davison, BL	Product of Example 1
Density, lbs./Cu. Ft.	46	46	42	43
Crush Strength, Dry, lbs.	17	22	25	20
Wet, lbs.	6	9	9	10
H <sub>2</sub> O Adsorption at 10% relative weight percent humidity lbs. H <sub>2</sub> O/Cu. Ft.	19.2	18.4	22.5	22.2
CO <sub>2</sub>	8.8	8.5	9.5	9.5
Adsorption at 250 mmHg, Room Temperature				
10 Min., Wt. %	11.2	-	13.9	13.4
Equil.,	12.7	10.0	15.7	15.3
Lbs. CO <sub>2</sub> /Cu. Ft.	5.8	4.6	6.6	6.6
Desorption Under Vacuum, Room Temperature				
5 Min., Wt. %	4.8	-	5.8	6.9
10 Min., Wt. %	5.8	-	6.9	8.4
15 Min., Wt. %	6.5	-	7.8	9.4
20 Min., Wt. %	7.0	-	8.5	10.2

It is apparent from a review of these data that the density of the product compared favourably with the density of the other products and that the wet crush strength was better than that of any of the commercially available products. The water adsorption at 10% relative humidity compared favourably with the Davison binderless product and was substantially better than the Davison and Linde R products. The desorption under vacuum was also greatly improved when compared to the other commercially available products.

*Example 3*

The product of run (a) of Example 1 was converted to the calcium form using the standard technique such as described in U.S. Patent 2,882,243. The product from the crystallization step that had been washed with hot water was exchanged with a calcium chloride solution. A total of 500 lbs of the sodium zeolite was mixed with a solution of 420 lbs of calcium chloride and 1500 lbs of water. The exchange was carried on for a period of 1 hour at 180°F and at the end of this time the zeolite was separated from the calcium chloride solution and the exchange was repeated. The final step was washing with hot water. The product was then dried and calcined at a temperature of 1000°F for 2 hours.

*Example 4*

The properties of the resulting 5Å molecular sieve were compared with the same products as in Example 2 except that each of the products was in the calcium form converted to the 5Å molecular sieve. The data are set out in Table II below.

Table II  
COMPARISON OF KEY PROPERTIES  
5A MOLECULAR SIEVES

	Davison, R	Linde, R	Davison, BL	Product of Example 3
Density, lbs./Cu. Ft.	42	45	42	43
Crush Strength, Dry, lbs.	13	9	18	26
Crush Strength, Wet, lbs.	5	6	10	11
H <sub>2</sub> O Adsorption at 10% weight percent relative humidity	16.5	15.9	18.4	20.3
Lbs. H <sub>2</sub> O/Cu. Ft.	6.9	7.2	7.6	8.7
n-Butane Adsorption at 760mmHg, Room Temperature				
10 min., Wt. %	—	—	11.9	10.5
Equil.,	10.6	10.3	12.2	11.7
Lbs. N-C <sub>4</sub> /Cu.Ft.	4.5	4.6	5.1	5.0
Desorption Under Vacuum, Room Temperature				
5 min., Wt. %	—	—	4.2	4.1
10 min., Wt. %	—	—	4.9	4.6
15 min., Wt. %	—	—	5.3	5.0
20 min., Wt. %	—	—	5.4	5.2
Iso-Butane Adsorption at 760mmHg, Room Temperature	0.56	0.26	0.10	0.43, 0.47

It is apparent from a review of these data that the water adsorption of the 5Å product of Example 3 at 10% relative humidity is substantially better than any of the other products. The isobutane adsorption is also substantially decreased compared with Davison Regular product, indicating reduction of non-discriminating surface.

5 WHAT WE CLAIM IS:- 5

1. A process for preparing extrudates of zeolite A which comprises the steps of:
  - (a) mixing metakaolin powder with a sufficient quantity of sodium hydroxide to provide 80 to 120% of the stoichiometric amount needed to convert the metakaolin to the zeolite;
  - (b) extruding the resultant mixture to form extrudates;
  - 10 (c) heating the extrudates at a temperature of 80 to 110°C for 2 to 8 hours to convert the mixture to the zeolite having a pore size of 4Å;
  - (d) washing to remove excess sodium hydroxide, and
  - (e) drying at 200 to 400°F to a moisture content of 5.0 to 15%, by weight and calcining at a temperature of 400 to 1100°F to moisture level of 1-5% by weight.
- 15 2. A process according to claim 1 wherein the sodium hydroxide is added in step (a) as a 30 to 55% by weight solution. 15
3. A process according to claim 1 or 2 wherein the metakaolin is mixed with a pilling aid before it is mixed with the sodium hydroxide in step (a).
4. A process according to claim 3 wherein the pilling aid is a long chain fatty acid.
- 20 5. A process according to any preceding claim, which further comprises ion-exchanging the 4Å product at some stage after step (d) with a solution of a calcium salt to produce a calcium form 5Å zeolite. 20
6. A process according to any preceding claim, which further comprises ion-exchanging the product at some stage after step (d) with a magnesium or rare earth salt solution.
- 25 7. A process according to any preceding claim, wherein said heating step (c) is effected in an aqueous solution containing 1 to 50% by weight sodium hydroxide. 25
8. A process according to claim 7 wherein the aqueous solution in which the heating step (c) is effected contains nucleation centres in an amount of 0.1 to 1% by weight of alumina in the metakaolin.
- 30 9. A process according to claim 1, substantially as described in run (a) or (b) of Example 1 or in Example 3. 30
10. Extrudates containing zeolite A when produced by a process according to any one of claims 1 to 9.

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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of  
the Original on a reduced scale*

